

IN THE UNITED STATES PATENT OFFICE

In re application of Hiroyuki MISHIMA
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For : PREPREG AND LAMINATE

I, Hiroyuki MISHIMA, declare that :

1. I have instructed experiments which are described in the attached report;

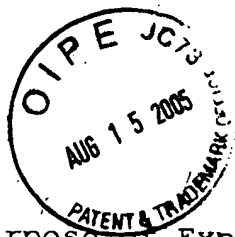
2. I am the coinventor of the present invention, and a staff member of the Technology Research Department of Electronics Material of Tokyo Works of Mitsubishi Gas Chemical Company, Inc., and I have studied the outstanding Official Action dated April 11, 2005.

3. I graduated from Tokyo Institute of Technology, the master's course in polymer chemistry course of Department of Technology in March 1989. I joined Mitsubishi Gas Chemical Company, Inc., in April 1989, and was attached to the Polymer Laboratories in April 1989, and was attached to the Technology Research Department of Electronics Material of Tokyo Works of Mitsubishi Gas Chemical Company, Inc., in July 1993, where I have been and am engaged in the study and development of resin composition for print circuit boards and the like.

4. All statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements and the like so made are punished by fines or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

The 3rd day of August, 2005

Hiroyuki MISHIMA



Experimental Report

1. Purpose of Experiment

To clarify a difference in quality characteristics between a copper-clad laminate using a heat-treated product of aluminum hydroxide disclosed by Brown et al. (W/O 98/31538) and a copper-clad laminate using a hydrothermal treated product of aluminum hydroxide used in the present invention, i.e., an aluminum hydroxide-boehmite composite.

2. Experimental Method

Samples

Sample A: Aluminum hydroxide-boehmite composite having a boehmite conversion rate of 11 % and obtained by hydrothermal treatment of aluminum hydroxide.

Sample B: Aluminum hydroxide-boehmite composite having a boehmite conversion rate of 18 % and obtained by hydrothermal treatment of aluminum hydroxide.

BS-40 (trade name, supplied by Kawai Lime Industry Co., Ltd.): Aluminum hydroxide-boehmite composite having a boehmite conversion rate of 39 % and obtained by hydrothermal treatment of aluminum hydroxide.

HIGILITE H-32 (trade name, supplied by Showa Denko K.K.) : Prepared by heating an aluminum hydroxide having an average particle diameter of 8 μm , a BET specific surface area of 2 m^2/g and an oil absorption of 32 $\text{ml}/100\text{g}$ in an electric oven operating at a temperature of 220 $^{\circ}\text{C}$ for 2 hours according to the example of Brown et al.

Table 1 shows the properties of the above samples.

(Table 1)

	Sample A	Sample B	BS-40	Heat-treated H-32
Average particle diameter (μm)	1.4	1.0	1.4	8.0
BET specific surface area (m^2/g)	No datum	6.6	6.1	7.9
Ignition loss (%)	33	31	27	33
Boehmite ratio (%) by X-ray diffraction	11	18	39	5

Example 1

60 parts by weight of a prepolymer (BT-2610, supplied by Mitsubishi Gas Chemical Company, Inc.) of bis(3,5-dimethyl-4-maleimidephenyl)methane and 2,2-bis(4-cyanatophenyl)propane, 40 parts by weight of a phenol novolak epoxy resin (N770, supplied by Dainippon Ink And Chemicals, Incorporated), and 0.5 part by weight of γ -glycidoxypopyltrimethoxysilane (A-187, supplied by Nihonunica Corporation) were dissolved in methyl ethyl ketone, and then 100 parts by weight of Sample A and 0.01 part by weight of zinc octylate were mixed with the resultant solution, to obtain a varnish.

The varnish was diluted with methyl ethyl ketone, the diluted varnish was impregnated into an E glass cloth having a thickness of 0.1 mm, and the impregnated cloth was dried under heat at 150 °C, to obtain prepregs having a resin content (including an inorganic filler) of 48 % by weight. Four sheets of the prepregs were stacked, 12 μ m thick electrolytic copper foils were disposed on the upper surface and the lower surface of the stacked prepregs, and the resultant set was pressed at a pressure of 30 kg/cm² at a temperature of 220 °C for 120 minutes, to obtain a copper-clad laminate having a thickness of 0.4 mm.

Example 2

A copper-clad laminate having a thickness of 0.4 mm was obtained in the same manner as in Example 1 except that 100 parts by weight of Sample A was replaced with 100 parts by weight of Sample B.

Example 3

A copper-clad laminate having a thickness of 0.4 mm was obtained in the same manner as in Example 1 except that 100 parts by weight of Sample A was replaced with 100 parts by weight of an aluminum hydroxide-boehmite composite (BS-40, supplied by Kawai Lime Industry Co., Ltd.).

Comparative Example 1

A varnish was obtained in the same manner as in Example 1 except that 100 parts by weight of Sample A was replaced with 100 parts by weight of a heat-treated product of aluminum hydroxide prepared by heat-treating aluminum hydroxide (HIGILITE H-32, supplied by Showa Denko K.K.) in a hot-air dryer at 220 °C for 2 hours and riddling the heat-treated aluminum hydroxide.

A copper-clad laminate having a thickness of 0.4 mm was obtained in the same manner as in Example 1 except that the above varnish was used.

3. Experimental results

Table 2 shows the evaluation results of the laminates obtained in Examples and Comparative Example.

	Appearance of laminate	Solder heat resistance 260°C, Dip	Insulation resistance D-6/100	Flame resistance (UL method)
Example 1	No appearance irregularities	20 minutes	$5 \times 10^{12} \Omega$	V-0
Example 2	No appearance irregularities	25 minutes	8×10^{12}	V-0
Example 3	No appearance irregularities	>30 minutes	1×10^{13}	V-0
Comparative Example 1	Appearance irregularities found	7 minutes	2×10^{12}	V-0

(Test Methods)

Appearance of laminate: Judged by visual observation after etching copper foils.

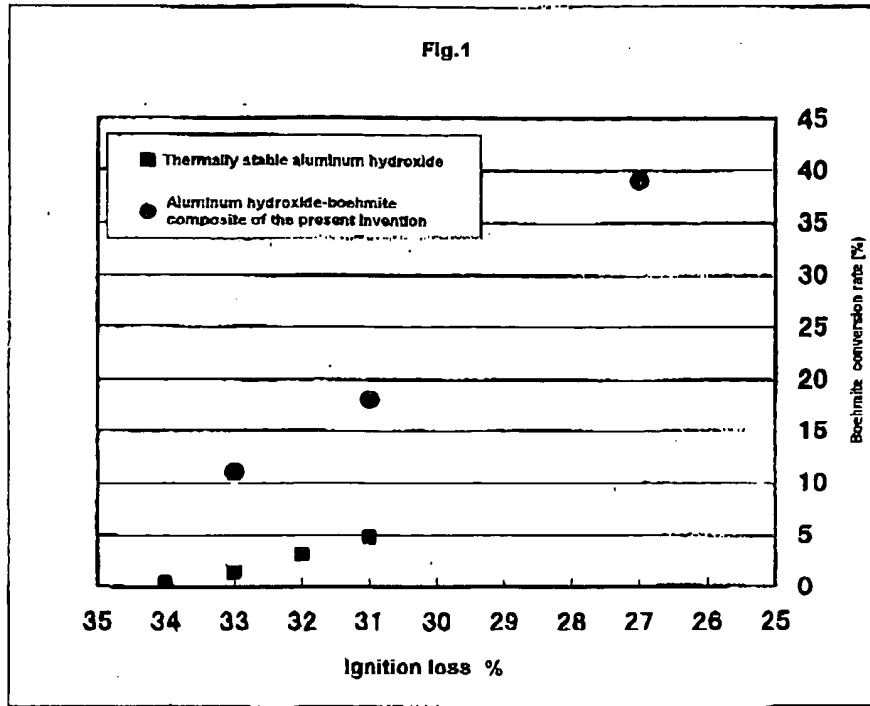
Solder heat resistance: According to JIS C6481.

Insulation resistance: According to JIS C6481.

Flame resistance: According to a UL94 vertical test method.

Photographs showing the appearances of the laminates obtained in Example 1 and Comparative Example 1 are attached.

Fig. 1 shows the relation of a boehmite conversion rate and an ignition loss, reported in Brown et al., and the relation of the aluminum hydroxide-boehmite composites obtained in the present Experimental Report, i.e., Sample A, Sample B and BS-40, and ignition losses.



	34	33	32	31	27
Thermally stable aluminum hydroxide	0.36	1.43	3.04	4.82	
Aluminum hydroxide-boehmite composite of the present invention		11		18	39

4. Conclusion

The aluminum hydroxide-boehmite composites obtained by hydrothermal treatment used in the present invention had a boehmite conversion rate of 11 %, calculated from X-ray diffraction, at an ignition loss of 33 % (Sample A), and a boehmite conversion rate of 18% at an ignition loss of 31 % (Sample B). The heat-treated product of aluminum hydroxide had a boehmite conversion rate of 5% at an ignition loss of 33 %. In comparison with the FIGURE 1 of WO98/31538, the above values of the aluminum hydroxide-boehmite composites obtained by hydrothermal treatment used in the present invention were similar to the curve 1 of the FIGURE 1 and the value of the heat-treated product of aluminum hydroxide was the same as the curve 4. Therefore, the aluminum

hydroxide-boehmite composite obtained by hydrothermal treatment used in the present invention tends to have a very high boehmite conversion rate unlike thermally stable aluminum hydroxide of the curve 4.

Accordingly, the aluminum hydroxide-boehmite composite, obtained by hydrothermal treatment, of the present invention has a boehmite ratio which is not lower than that of the heat-treated product of aluminum hydroxide and it is completely different from the thermally stable aluminum hydroxide of WO 98/31538.

In addition, as shown in the attached photographs, the laminate using the aluminum hydroxide-boehmite composite obtained by hydrothermal treatment used in the present invention could be molded without resin flow irregularities. In contrast, the laminate using the heat-treated product of aluminum hydroxide had resin flow irregularities. Therefore, it is also obvious that there is a difference in the affinity to a resin.